



Short communication

Synthesis and electrochemical properties of MoO₃/C composite as anode material for lithium-ion batteriesQing Xia^a, Hailei Zhao^{a,b,*}, Zhihong Du^a, Jie Wang^a, Tianhou Zhang^{a,b}, Jing Wang^a, Pengpeng Lv^a^a School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China^b Beijing Key Lab of New Energy Materials and Technology, Beijing 100083, China

H I G H L I G H T S

- ▶ The MoO₃/C nano-composite is synthesized by a one-pot citric-nitrate method.
- ▶ Carbon is *in situ* formed in the MoO₃ matrix.
- ▶ MoO₃/C composite powder presents a core–shell structure feature.
- ▶ The MoO₃/C composite exhibits specific capacity of ca. 500 mAh g^{−1} after 100 cycles.
- ▶ The method is of general applicability for other oxide/carbon anode materials.

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MoO₃ has been reported as attractive candidate of anode materials for lithium-ion batteries. In this article, a facile one-pot citric-nitrate method is proposed to synthesize MoO₃/C nano-composite, which is of general applicability for other oxide/carbon anode materials. The synthesized MoO₃/C presents a core–shell structure feature with a thin carbon layer coating on the surface of nano-crystalline MoO₃. The MoO₃/C anode exhibits superior electrochemical performance, a specific capacity of about 500 mAh g^{−1} in the voltage range of 0.01–3.0 V vs. Li/Li⁺ can be maintained after 100 cycles.

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1. Introduction

Lithium-ion batteries (LIBs) have become the dominant power sources for portable electronic devices because of their high energy density and long cycle life. Although carbonaceous materials are still the accepted anode used in the majority of commercial lithium-ion batteries, a vast amount of research has been devoted to developing new anode materials with higher capacity and good safety in order to meet the growing demands of high performance battery for electric vehicles and energy storage systems [1]. In the past several years, many new anode materials have been reported, such as Si- [2], Sn- [3] and Sb-based [4] materials.

Transition-metal oxides also show high specific capacity toward to lithium ion intercalation when the particle size is decreased to nanoscale [5,6]. Among various metal oxides, MoO₃ is an attractive anode material for LIBs. There are three polymorphs of MoO₃, orthorhombic α -MoO₃, monoclinic β -MoO₃ and hexagonal h-MoO₃ [7]. The α -phase has a double-layered structure along the [010] direction with covalent bonds inside the dense layer and van der Waals forces between the adjacent double-layers [7,8]. Due to the anisotropic layered structure and the ability of the molybdenum ion to change its oxidation state, α -MoO₃ demonstrates a promising performance as anode materials for LIBs. Based on the mechanism that six lithium ions can be accommodated by 1 mol MoO₃, a theoretical capacity of 1117 mAh g^{−1} is expected [9].

As an alternative anode material, MoO₃ has attracted much attention recent years. Previous reports demonstrated that bulk MoO₃ powder usually displayed a lower specific capacity with a much poor cycling performance, while nano-sized MoO₃ exhibited higher capacity and good cycling stability [10–12]. L.A. Riely

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et al. [10] employed hot wire chemical vapor deposition to synthesize MoO_3 nanoparticles, which showed a near-theoretical reversible capacity of about 1050 mAh g^{-1} . The incorporation of carbon into MoO_3 has been proved to be capable of enhancing the electrochemical properties and improving the cycling stability of electrode. Carbon-coated nanobelts with a diameter of 150 nm and a length of 5–8 μm were synthesized by M.F. Hassan et al. via a hydrothermal route, which exhibited a significantly high capacity and good cycling stability compared to the pure MoO_3 nanobelts [13]. The capacity of the C– MoO_3 nanobelts maintained at 1064 mAh g^{-1} after 50 cycles at a current rate of 0.1 C. T. Tao et al. prepared MoO_3 -carbon nanocomposite by ball-milling a mixture of MoO_3 and graphite for 100 h [14]. They found that a proper content of carbon can remarkably enhance the electrochemical performance. The MoO_3/C nanocomposite with a weight ratio of 1:1 displayed a reversible capacity as high as 700 mAh g^{-1} at 0.2 C rate after 120 cycles. Apart from increasing the conductivity of electrode, the carbon component can buffer the big volume change, which is about 104% [11], caused by the lithiation/delithiation of MoO_3 and prevent the local loss of contact between active particles during charge/discharge process, therefore improving the cycling stability of electrode.

In this work, an alternative method of preparing $\text{MoO}_3/\text{carbon}$ nanocomposite is proposed. The nanocomposite MoO_3/C was synthesized by a facile one-pot route, where the carbon was introduced *in situ*, and therefore uniformly dispersed in MoO_3 host, forming a homogeneous structure. The structure characteristics and electrochemical properties of MoO_3/C were evaluated and compared with the pure MoO_3 material.

2. Experimental

The MoO_3/C powders were synthesized by a one-pot citric-nitrate method. Ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was used as molybdenum source while sucrose as carbon source. Firstly, an amount of 1.766 g ammonium molybdate, 4.203 g citric acid and 1.029 g sucrose were dissolved in deionized water. The ratio of MoO_3 to carbon (from sucrose) was set as 10:3 in weight, corresponding to 23 wt. % carbon. Then 4 ml aquafortis (HNO_3) and 1 ml ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were added into the solution, followed by magnetically stirring for several minutes, until a settled homogeneous solution was formed. After that, the solution was water-bathed to get hydrosol. The hydrosol was transferred into evaporating dish and then dried at 80°C in an oven to obtain xerogel. The temperature of the oven was then increased to 250°C to make the gel self-propagating to obtain the precursor. Afterward, the precursor was placed in ceramic boat and calcined at 500°C for 3 h in nitrogen gas to get MoO_3/C powder. According to the element analysis, the actual carbon content in the synthesized MoO_3/C is 28 wt. %, slightly higher than the designed carbon content. The extra carbon comes probably from the pyrolyzed of citric acid. The pure MoO_3 powder was fabricated by a same procedure without sucrose addition and, especially, the precursor was heat-treated in air at the same temperature.

The phases of the samples were identified by X-ray diffraction (XRD, Rigaku, D/max-A, $\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$). The morphology of as-prepared powder was observed by a field-emission scanning electron microscope (FE-SEM, SUPRA55) and a transmission electron microscope (HRTEM, JEM-2000FX). Infrared spectrum of the samples was recorded on a Fourier transform infrared spectroscope (FTIR, NEXUS FT-IR670) in the range of $400\text{--}4000 \text{ cm}^{-1}$.

The electrochemical properties were evaluated by using two-electrode half-cell with the synthesized MoO_3/C or MoO_3 as working electrode, lithium foil as the counter electrode, and the porous polypropylene film (Celgard 2400) as the separator. The

working electrodes was prepared by mixing MoO_3/C or MoO_3 active material, acetylene black and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidinone (NMP) with a mass ratio of 70:15:15 to form homogeneous slurry, which was then pasted onto copper foil. The copper foil with electrode materials was punched into circular discs with a diameter of 8 mm for cells assemble, and then dried at 120°C in a vacuum oven for 24 h. The mass of active materials in each disc was about 1.5 mg cm^{-2} . The electrolyte consisted of 1 M LiPF_6 in a mixture solution of ethylene carbonate (EC), ethylmethyl carbonate (EMC), and dimethyl carbonate (DMC) (1:1:1 in vol.). The cells were assembled in an Ar-filled glove box. The cycling performance was carried out at different current densities in the voltage range of 0.01–3.0 V vs. Li/Li^+ with LAND BT-10 tester (Wuhan, China). Cyclic voltammogram measurements were performed with an electrochemical working station at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.01–3.0 V vs. Li/Li^+ .

3. Results and discussion

Fig. 1 (a) shows the XRD patterns of the synthesized pure MoO_3 and MoO_3/C , respectively. The pattern of pure MoO_3 can be indexed well with $\alpha\text{-MoO}_3$ (PDF, 65–2421), giving evidence of that pure MoO_3 can be easily synthesized by citric-nitrate method. The broad peak of MoO_3/C powder with high background indicates that the synthesized MoO_3/C composite has either amorphous or nanocrystalline structure. There is no peak corresponding to MoO_3

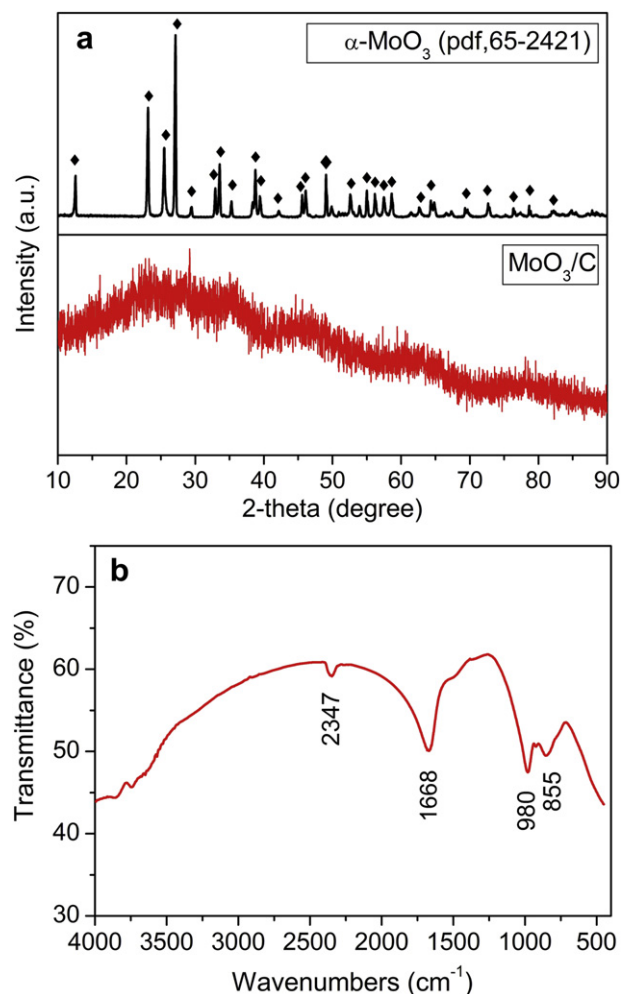


Fig. 1. (a) XRD patterns of pure MoO_3 and MoO_3/C powders. (b) FTIR spectrum of MoO_3/C .

being observed. The existence of carbon may prevent the grain-growth of MoO_3 during the heat treatment, thereby resulting in the formation of nano-sized MoO_3 particles, which exhibit amorphous feature in XRD pattern. To characterize the detailed structure, the MoO_3/C powder was subjected to the FTIR examination. The result is shown in Fig. 1 (b). The peaks nearby 855 cm^{-1} and 980 cm^{-1} are assignable to the vibration of Mo–O bond [15], while the peaks centered at 1668 and 2347 cm^{-1} are attributed to C=C bond and carbon dioxide [16], respectively. This demonstrates that molybdenum oxide and carbon were formed in the mixture. The CO_2 comes mainly from the carbonization of organic groups in precursor during calcination process, which is absorbed on the surface of composite particles.

The SEM images of MoO_3/C and MoO_3 powders are shown in Fig. 2 (a) and (b). The MoO_3/C powder displays an irregular particle shape, while MoO_3 presents a well-defined short-bar like particle morphology with a relatively uniform particle size distribution. The irregular and large particle morphology of MoO_3/C powder is mainly due to the formation of carbon network in the material,

which is frequently found in pyrolyzed carbon containing materials [17,18]. Careful inspection on the large particles of particle MoO_3/C indicates that a lot of small pores exist in the matrix, as depicted in the inset of Fig. 2 (a). The formation of such structure is attributable to the generation of large quantity of gases, carbon oxides and nitrogen oxides, in the sample preparation processes and the viscous feature of sucrose before carbonization. These pores may help to accommodate the volume change of MoO_3/C electrode during lithiation/delithiation process, and thus improve the cycling stability of electrode. Energy dispersive X-ray (EDX) analysis on MoO_3/C powder reveals that the atomic ratio of Mo/O is 25.02:74.98 (Fig. 2c), very close to 1:3, which is a direct evidence to identify the molybdenum oxide as MoO_3 .

To get insight into the detailed structural characteristics, the sample MoO_3/C was further subjected to a HR-TEM observation. The selected area diffraction image acquired from the lattice area is shown in Fig. 2 (d). Two distinct parts are observed, well-ordered and disordered areas. Within the ordered part, two different interplanar spacings of 0.247 and 0.352 nm could be identified,

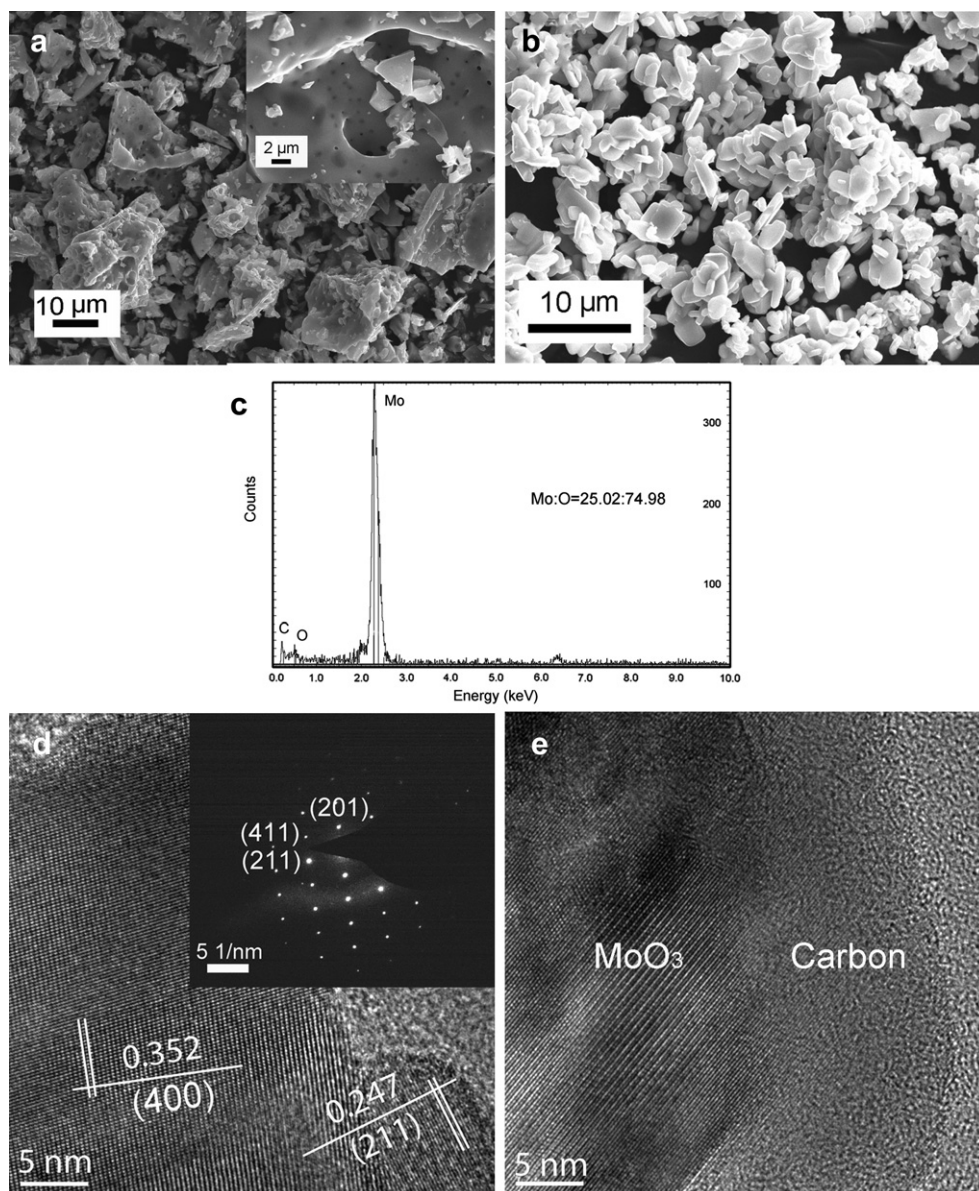


Fig. 2. SEM micrographs of MoO_3/C (inset: the magnified image of the sample) (a) and MoO_3 (b). EDX spectrum of MoO_3/C (c). HR-TEM micrographs of the inside (inset: selected area diffraction image) (d) and the edge of MoO_3/C particle (e).

which agree well to the calculated value based on (211) and (400) planes of MoO_3 . The disordered part should be ascribed to the carbon component. The selected area diffraction for the ordered part is presented in the inset of Fig. 2 (d), which can be indexed well with the structure of MoO_3 (PDF, 65–2421). This information reveals that the MoO_3/C particle is actually composed of nano-sized crystalline MoO_3 and amorphous carbon. Fig. 2 (e) gives a much clear morphology of MoO_3/C particle, where a thin carbon layer about 10–15 nm is coated on the MoO_3 surface, indicating a core-shell structure feature. These results demonstrate that the MoO_3 and MoO_3/C powders can be easily prepared by the employed one-pot citric-nitrate method, which is simple and productive, and thus suitable for large scale production.

The cyclic behaviors of the MoO_3/C and pure MoO_3 electrodes at 100 mA g^{-1} rate between 0.01 and 3.0 V vs. Li^+/Li are illustrated in Fig. 3 (a). Compared to pure MoO_3 electrode, MoO_3/C shows much higher specific capacity and good cycling stability. The better electrochemical performance of MoO_3/C electrode is mainly attributed to the presence of amorphous carbon, which provides electronic conduction channels and further facilitates the electrode reaction process. MoO_3 has been found to experience a volume expansion during lithium intercalation [19], which may cause the electrode to crack and thus lose some electronic contact between

active particles, bringing poor cycling stability and low capacity retention, as reflected by sample MoO_3 . Although the prepared MoO_3 electrode exhibits a high first discharge/charge capacity of 1350.4 and 805.2 mAh g^{-1} , it decreases very fast with cycle. After 100 cycles, only 59.7 mAh g^{-1} is remained. This is consistent with other reported result [13].

With respect to the MoO_3/C anode material, it exhibits high discharge capacity of 1260 mAh g^{-1} at the current density of 100 mA g^{-1} with initial coulombic efficiency of 72.5%. The irreversible capacity mainly results from the formation of a solid electrolyte interphase (SEI) layer and the incomplete conversion reaction from the MoO_3 and carbon components [14,20,21]. The first charge specific capacity is 913.4 mAh g^{-1} , which is much closer to the theoretical capacity of MoO_3/C composite with 28 wt. % carbon (908.4 mAh g^{-1}). The capacity of MoO_3/C electrode decreases very fast during the first 20 cycles and then reaches a relatively stable status. The fast degradation of electrode at the beginning of cycling is mainly due to the pulverization of active MoO_3 due to the large volume change. The good cycling performance in the subsequent cycles can be attributed to the existence of carbon. The carbon component in the MoO_3/C composite is generated *in situ*, therefore it disperses uniformly with MoO_3 particles. Carbon component can accommodate in certain extent the volume change induced by active MoO_3 during cycling and maintain the structural integrity, improving the cycling performance of the electrode. Moreover, the amorphous carbon can prevent the electrochemical aggregation of nano-sized MoO_3 particles and keep the high activity of nano-sized particle toward the insertion of lithium ions. The specific capacity of MoO_3/C electrode still retains at about 500 mAh g^{-1} after 100 cycles. Compared to the result reported in literature [14], the lower specific capacity of the synthesized MoO_3/C is probably owing to the relatively larger particle size of MoO_3 in this work. After further optimization in synthesis parameters, a smaller MoO_3 particle dispersed with carbon and a better electrochemical performance can be expected.

The MoO_3/C electrode was cycled stepwise at different current densities to evaluate the rate capability. The charge/discharge voltage curves at different rates are plotted in Fig. 3 (b). They all exhibit smooth voltage profiles, unequivocally revealing the nano-structural feature of MoO_3/C composite, which can be elucidated by the surface energy described for many nano-systems [22,23]. The specific capacity of MoO_3/C composite anode material decreases with increasing current density, which is ascribable to the electrode polarization. A stable capacity of 530 mAh g^{-1} is still delivered at 500 mA g^{-1} , reaching nearly 76% of the capacity at 100 mA g^{-1} . When the rate backs to the value of 100 mA g^{-1} , the reversible capacity still maintains at 695 mAh g^{-1} after 56 cycles. This demonstrates the good rate-capability of MoO_3/C composite.

The CV curves of MoO_3/C electrode for first three cycles are presented in Fig. 3 (c). The broad peak characteristic suggests the nano-structural feature of the active material. The cathodic peak centered at about 0.75 V corresponds to the formation of a SEI layer, which disappears in the following cycles. The broad peak down to 0.01 V is related to the lithiation reaction of MoO_3 . This peak shows a larger area in the first cycle than in the following cycles, indicating a part of irreversible conversion. The anodic peak centered at 1.4 V can be assigned to the extraction process of lithium from its oxides. Besides the first cycle, the following cycles display overlapped curves, indicating the high reversibility of electrode reaction.

4. Conclusions

The composite of MoO_3/C was prepared by a simple one-pot citric-nitrate method with sucrose as carbon source, which is composed of nano-crystalline MoO_3 and amorphous carbon.

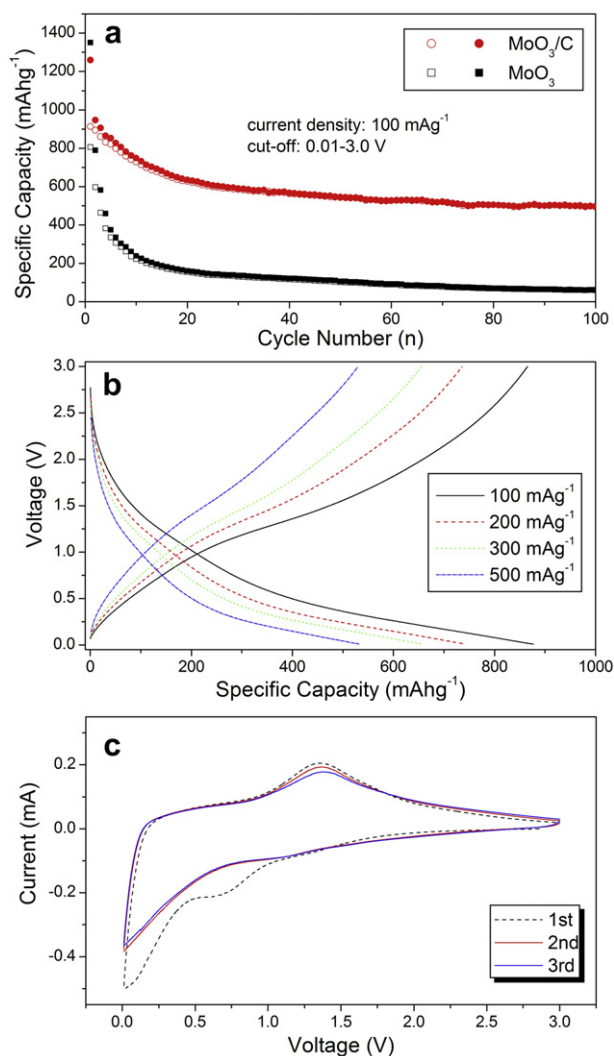


Fig. 3. (a) Cycling performance of MoO_3/C and MoO_3 electrodes. (b) Rate capability of MoO_3/C electrode. (c) CV curves of the MoO_3/C electrode for the first three cycles.

Because carbon is *in situ* formed, it disperses homogeneously with nanoparticles MoO₃. HR-TEM observation suggests that a thin carbon layer with thickness of 10–15 nm exists on the particle surface of MoO₃, forming a core–shell structure. With the same method but without sucrose addition, the well-defined micro-sized pure MoO₃ powder with short-bar like particle morphology was synthesized. As anode materials for lithium-ion batteries, the MoO₃/C composite exhibits higher specific capacity and superior cycling stability compared to the pure MoO₃ material. The uniformly existing of carbon can enhance the electrode reaction and maintain the electrode integrity. The MoO₃/C composite retains a high reversible capacity of about 500 mAh g^{−1} in the voltage range of 0.01–3.0 V vs. Li/Li⁺ till 100 cycles. Considering the simplicity, the employed one-pot citric-nitrate method is a promising approach to synthesize carbon-containing nano-composite as electrode material for lithium-ion batteries.

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